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Note

Thermodynamic data for H-complexes of some pyridine bases with lower alcohols as determined from gas–liquid partition chromatographic measurements

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Gas–liquid partition chromatography (GLPC) is an important physico-chemical method for determining the parameters that characterize the solubility of a substance, the liquid–vapour equilibrium, the intermolecular interaction and other phenomena[1,2]. In using this method to determine the equilibrium constant, K_A, of a molecular complexation process

$$A + B \rightleftarrows AB \qquad (1)$$

one should measure the retention data for a solute B (chromatographed substance) using a column filled with a mixed stationary phase containing an active component A. Usually the stationary phase consists of the complex-forming component A dissolved in an inert (as regards complexation) component S. In many instances the dependence of the retention data relating to the composition of the mixed stationary phase are non-linear and are analysed in terms of energetic effects due to mixing of the components that form the phase. However, when a particular property increases linearly with increasing concentration of the complex-forming compound A, then one can evaluate the complexation constant, K_A, of eqn. 1[1–10]. The following equation that enables one to do this was derived by Bradford *et al.*[3], Littlewood and Willmott[4], Purnell[5] and Soczewiński and Gołkiewicz[9] by relating the retention data to the law of mass action:

$$K = K^0 (1 + K_A x_A) \qquad (2)$$

where K is the partition coefficient of a solute (B) between a mixed stationary phase, in which the concentration of the complex-forming component A is c_A, and the gas phase. In this paper the molar fraction, x_A, is used as the concentration unit. K^0 is the partition coefficient for $x_A = 0$, *i.e.*, for the distribution of the component B between the pure non-polar component (S) of the stationary phase and the gas phase. K_A is the equilibrium constant of the complexation (eqn. 1) and is expressed in the unit reciprocal to that of the concentration of component A.

K_A can be evaluated by plotting the ratio K/K^0 against x_A, when the slope of the dependence taken at $x_A = 0$ is equal to K_A. In this study x_A was varied over a

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fairly wide range (see Tables II–IV) to establish whether the linearity of eqn. 2 is obeyed. A deviation was usually observed for higher x_A values, so the K_A value was always determined from the small x_A value portion of the graphs.

The K_A values determined in this way assume that the activity coefficients approach unity with dilution of the solutions. The K_A values are solvent dependent. The solvent used here (squalane) is one of the most inert, so the data determined represent well the complexation process between the species A and B. For a thorough discussion of the state of reference for K_A determinations, see ref. 2.

From the K_A value one can calculate the differential standard free enthalpy, ΔG, of the complexation process:

$$\Delta G = -RT \ln K_A \tag{3}$$

The temperature dependence of K_A gives through the van 't Hoff isobar equation (eqn. 4) the enthalpy of complexation, ΔH:

$$\left(\frac{\partial \ln K_A}{\partial T}\right)_p = \frac{\Delta H}{RT^2} \tag{4}$$

where R and T have their usual significance. After integrating with the assumption that ΔH is constant and substituting numerical data, where possible, one can obtain the equation

$$\log K_A = -\frac{\Delta H}{19.1546} \cdot \frac{1}{T} + \text{constant} \tag{5}$$

(ΔH is in J/mol). Hence ΔH can be determined from the slope of the straight line of $\log K_A$ versus $1/T$. Eqn. 2 can be extended to systems in which, in addition to 1:1 complex, a 1:2 molecular complex is also formed[10].

The gas chromatographic method discussed here has been used for determining various physico-chemical data of many systems. It has mainly been applied for characterizing the most popular multi-component stationary phases[4,9,11–15]. Haky and Muschik[16] used the method for investigating the properties of liquid crystalline mixtures. Many papers have been devoted to measuring the physico-chemical constants of molecular donor–acceptor complexes formed between a solute introduced on to a column and a complex-forming component of the stationary phase. These thermodynamic data were determined for the complexes formed by derivatives of heteroaromatics with dibutyltetrachloronaphthalate[11] and of tetradecylamine with chloroform and methanol[10].

The method has also been used for investigations of interactions between volatile compounds with polymers[17,18] and products of coal liquefication[19] and also between bis(ethylhexyl)tetrachlorophthalate and volatile solvents[12].

The aim of this work was the determination of the quilibrium constants and the enthalphy of 1:1 molecular complexes formed between some pyridine bases and lower aliphatic alcohols.

EXPERIMENTAL

A two-component stationary phase was used, consisting of a pyridine base (quinoline, isoquinoline, acridine or 2,6-dibromopyridine) and squalane, the latter serving as an inert solvent. The weight ratio between the pyridine base and squalane in the stationary phase was 1:7, 1:5, 1:3, 1:1 or 3:1.

Each of the mixed stationary phases was introduced onto the support (Fluoropak, 40–60 mesh) in the weight ratio 1:10. The stainless-steel column (1 m × 4 mm I.D.) was filled with the packing, then heated at 343.15°K (70°C) for 20 h with nitrogen passing through at a flow-rate (measured with a bubble flow meter) of 40 cm^3/min. The inlet pressure was measured with a mercury manometer. The retention time was measured at 318.15, 328.15 and 338.15°K (45, 55 and 65°C) at a nitrogen flow-rate of 40 cm^3/min. Methanol, ethanol or *n*-propanol was introduced on the top of the column (0.2–1.2 μl) and then the retention data were extrapolated to zero volume of the sample. For all the measurements a Giede (G.D.R.) Type GCHF 18.3 instrument equipped with a katharometer was used. The density of the stationary phases was measured with a pyknometer. The data obtained are given in Table I.

RESULTS AND DISCUSSION

The results obtained are summarized in Tables II–V.

When the stationary phase contained quinoline, isoquinoline or 2,6-dibromopyridine (component A) then the retention data (retention time, specific retention volume, partition coefficient) increased with increase in the concentration of component A, x_A, (Tables II–IV). The dependence was linear with a slight deviation for higher x_A values.

This behaviour indicated 1:1 molecular complex formation between solute B and component A of the mixed stationary phase. The calculated thermodynamic data (equilibrium constant, K_A, and enthalpy, ΔH) of the complexation are also given in Tables II–IV. Treatment of experimental data in this way was not possible for the acridine–aliphatic alcohols systems, as the relationship between the retention data

TABLE I

PROPERTIES OF THE LIQUID STATIONARY PHASES

No.	*Stationary phase*	*Composition*									
		1		*2*		*3*		*4*		*5*	
		Weight ratio	x_A*	*Weight ratio*	x_A	*Weight ratio*	x_A	*Weight ratio*	x_A	*Weight ratio*	x_A
1	Quinoline–squalane	1:7	0.32	1:5	0.40	1:3	0.52	1:1	0.77	3:1	0.91
2	Isoquinoline–squalane	1:7	0.32	1:5	0.40	1:3	0.52	1:1	0.77	3:1	0.91
3	2,6-Dibromopyridine–squalane	1:7	0.20	1:5	0.26	1:3	0.37	1:1	0.64	3:1	0.84
4	Acridine–squalane					1:3	0.44	1:1	0.70	3:1	0.88

* x_A = Molar fraction of component A in the stationary phase.

TABLE II

PARTITION COEFFICIENT, K, EQUILIBRIUM CONSTANT, K_A, AND FORMATION ENTHALPY, ΔH, FOR THE SYSTEMS WITH A STATIONARY PHASE CONSISTING OF QUINOLINE AS THE COMPLEX-FORMING COMOPONENT, A, DISSOLVED IN SQUALANE AT 318.15, 328.15 AND 338.15°K (45, 55 AND 65°C)

Complex-forming substance (solute B)	K															K_A			$-\Delta H$ (kJ/mol)
	$x_A^* = 0.32$			$x_A = 0.40$			$x_A = 0.52$			$x_A = 0.77$			$x_A = 0.91$			45°C	55°C	65°C	
	45°C	55°C	65°C	45°C	55°C	65°C	45°C	55°C	65°C	45°C	55°C	65°C	45°C	55°C	65°C				
Methanol	74.5	33.3	12.0	89.5	38.8	13.8	108.6	46.6	16.0	149.1	64.4	21.8	172.5	73.3	25.0	7.8	6.2	5.1	18.4
Ethanol	175.1	98.6	54.5	203.4	116.2	63.6	248.6	140.8	74.9	339.0	193.6	99.9	389.8	221.8	113.5	6.5	5.8	4.4	17.1
n-Propanol	407.3	247.1	159.8	458.2	280.7	183.8	543.0	325.7	215.7	712.7	426.7	271.7	814.6	494.1	311.6	4.2	3.7	3.1	12.5

TABLE III

RESULTS FOR SYSTEMS CONTAINING ISOQUINOLINE

Symbols as in Table II.

Complex-forming substance (solute B)	K															K_A			$-\Delta H$ (kJ/mol)
	$x_A^* = 0.32$			$x_A = 0.40$			$x_A = 0.52$			$x_A = 0.77$			$x_A = 0.91$			45°C	55°C	65°C	
	45°C	55°C	65°C	45°C	55°C	65°C	45°C	55°C	65°C	45°C	55°C	65°C	45°C	55°C	65°C				
Methanol	83.1	40.0	12.5	100.1	47.7	14.7	123.5	58.8	17.8	172.5	81.0	24.5	200.2	93.2	28.1	9.2	8.1	5.8	20.0
Ethanol	192.1	109.1	61.3	226.0	126.7	68.1	276.8	154.9	84.0	384.2	211.2	113.5	446.4	242.9	129.4	7.6	6.5	5.2	16.3
n-Propanol	526.1	247.1	167.8	610.9	292.0	191.8	746.7	359.4	223.7	1018.2	460.4	295.6	1170.9	527.8	335.6	6.5	4.1	3.5	15.8

TABLE IV

RESULTS FOR SYSTEMS CONTAINING 2,6-DIBROMOPYRIDINE

Symbols as in Table II

Complex-forming substance (solute B)	*K*															*K_A*			*$-\Delta H$ (kJ/mol)*
	x_A^* = 0.20			*x_A = 0.26*			*x_A = 0.37*			*x_A = 0.64*			*x_A = 0.84*			*45°C*	*55°C*	*65°C*	
	45°C	*55°C*	*65°C*	*45°C*	*55°C*	*65°C*	*45°C*	*55°C*	*65°C*	*45°C*	*55°C*	*65°C*	*45°C*	*55°C*	*65°C*				
Methanol	63.4	32.8	9.4	83.9	39.4	10.9	110.3	51.3	13.7	175.3	80.7	20.4	223.5	102.5	25.4	11.3	9.8	5.6	30.9
Ethanol	169.5	95.0	47.7	203.4	113.0	55.2	265.5	145.9	68.9	418.1	226.7	102.6	531.1	286.5	127.6	10.0	8.5	5.5	26.3
n-Propanol	441.2	258.3	164.6	522.7	302.1	190.0	672.0	382.4	236.6	1038.6	579.5	350.9	1310.1	725.5	435.6	8.0	6.5	5.3	18.0

TABLE V

PARTITION COEFFICIENT, K, AND ENTHALPY OF SOLUTION, ΔH, OF THE SOLUTE IN THE MIXED STATIONARY PHASE ACRIDINE–SQUALANE AT 318.15, 328.15 AND 338.15°K (45, 55 AND 65°C)

Solute B	*K*									*−ΔH (kJ/mol)*		
	x_A^* = 0.44			x_A = 0.70			x_A = 0.88			x_A = 0.44	x_A = 0.70	x_A = 0.88
	45°C	55°C	65°C	45°C	55°C	65°C	45°C	55°C	65°C			
Methanol	27.4	22.4	16.2	32.4	22.8	16.4	28.0	21.4	15.0	23.0	29.8	28.1
Ethanol	70.0	50.6	36.0	69.8	49.8	40.6	48.2	35.4	29.2	29.1	23.6	21.8
n-Propanol	200.6	148.6	104.2	197.6	152.4	110.4	126.0	97.0	71.6	28.6	25.5	24.7

* x_A = Molar fraction of acridine in the mixed stationary phase.

and the stationary phase composition was not linear and there was no evidence of molecular complex formation.Therefore, for these systems only the enthalpy of solution of the alcohols was determined (Table V). All the calculations were made by the least-squares method. The retention parameters measured and as a consequence the thermodynamic data for the systems studied depend on the molecular properties (mainly the hydrogen-bonding properties) of both complex-forming components, *i.e.*, A and B.

The highest K_A and ΔH values were found for the systems that contained methanol and the lowest for those containing *n*-propanol. This is consistent with the molecular structure of the alcohols, resulting in the greatest acidity for methanol and lower acidities for higher homologues[20]. Comparing the K_A and ΔH data for systems that differ only in the electron-donor component (A) of the complex molecule, one can see that the highest values were obtained for 2,6-dibromopyridine and the lowest for quinoline. This is again consistent with the basicity and steric properties of component A. Similar conclusions were drawn from other, mainly dielectric, studies[21,22] of the H-complexing properties of pyridine bases. For example, using a dielectric method the equilibrium constant at 298.15°K (25°C) was measured for the systems quinoline–*tert.*-butanol and isoquinoline–*tert.*-butanol in benzene and were K_A = 9.0 ± 1.0 and 21.4 ± 3.0 (molar fraction)$^{-1}$, respectively. These values are of the same order of magnitude as those obtained chromatographically in this work (Tables II en III). The differences are due to the differences in the temperature, medium (solvent) and alcohol used and pecularities of the measuring techniques (*i.e.*, dipole moment and GLPC measurements).

The lack of complex formation for the systems containing acridine seems to be due to the two benzoid rings adjacent to the central heteroaromatic ring.

REFERENCES

1 T. Czajkowska, in A. Waksmundzki (Editor), *Zastosowanie Chromatografii Gazowej w Badaniach Fizykochemicznych*, Ossolineum, Wrocław, 1974.
2 J. R. Condor and C. J. Young, *Physicochemical Measurement by Gas Chromatography*, Wiley, Chichester, New York, 1979, pp. 235–239.
3 B. W. Bradford, D. Harvey and D. B. Chaklkey, *J. Inst. Petrol.*, 41 (1955) 80.
4 A. B. Littlewood and F. W. Willmott, *Anal. Chem.*, 38 (1966) 1031.

5 J. H. Purnell, in A. B. Littlewood (Editor), *Gas Chromatography 1967*, Institute of Petroleum, London, 1967.
6 D. F. Cadogan and J. H. Purnell, *J. Chem. Soc. A*, (1968) 2133.
7 D. F. Cadogen and J. H. Purnell, *J. Phys. Chem.*, 73 (1969) 4389.
8 C. Eon, C. Pommier and G. Guiochon, *Chromatographia*, 4 (1971) 235.
9 E. Soczewiński and W. Gołkiewicz, *Chromatographia*, 4 (1971) 501.
10 T. Czajkowska and A. Waksmundzki, *J. Chromatogr.*, 119 (1976) 91.
11 C. Eon, C. Pommier and G. Guiochon, *Chromatographia*, 4 (1971) 241.
12 T. Czajkowska, *J. Chromatogr.*, 243 (1982) 245.
13 A. Waksmundzki and T. Czajkowska, *Ann. Soc. Chim. Pol.*, 47 (1973) 1909.
14 M. W. P. Harbison, R. J. Laub, D. E. Martire, J. H. Purnell and P. S. Williams, *J. Phys. Chem.*, 83 (1979) 1262.
15 E. L. Arancibia and J. A. Catoggio, *J. Chromatogr.* 238 (1982) 281.
16 J. E. Haky and G. M. Muschik, *J. Chromatogr.*, 238 (1982) 367.
17 A. A. Tager, T. J. Kiryllowa and T. V. Ikanina, *Vysokomol. Soedin., Ser. A*, 20 (1978) 2543.
18 V. G. Berezkin, V. R. Aliskoyer and J. B. Niemirovskaya, *Gas Chromatography of Polymers (Journal of Chromatography Library*, Vol. 10), Elsevier, Amsterdam, 1977, pp. 195–223.
19 Z. Kopacka-Kozak, to be published.
20 W. Wacławek, *Dielektryczne i Spektralne Badania Asocjatów Molekularnych*, Wydawnictwa Politechniki Warszawskiej, Warsaw, 1973.
21 A. Domagała and W. Wacławek, in preparation.
22 A. Domagała, *Ph.D. Thesis*, Wrocław University, Wrocław, 1983.